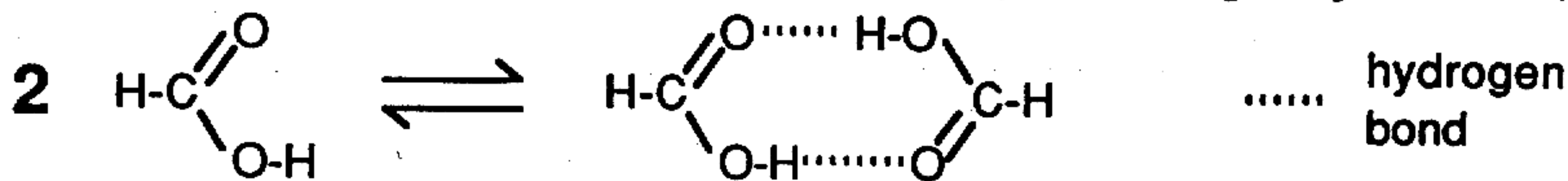


Name key

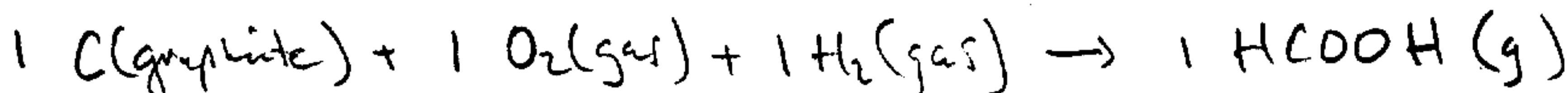
1. The following thermodynamic data have been tabulated for the gas phase reaction shown below (dashed lines represent hydrogen bonds):

 $\Delta H_f^\circ$  $S_f^\circ$ 

m	HCOOH (g)	-362.63 kJ/mol	251.0 J/mol K
d	(HCOOH) <sub>2</sub> (g)	-785.34 kJ/mol	347.7 J/mol K

a) To what hypothetical reaction does  $\Delta H_f^\circ$  of HCOOH (g) refer ?  
(specify exactly)

all at 1 atm, 298 K



b) Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the gas phase dimerization at 298 K. Is the formation of dimer spontaneous under these conditions?

$$\Delta H^\circ = \Delta H_f^\circ(d) - 2 \Delta H_f^\circ(m) = -60.08 \text{ kJ/mol}$$

$$\Delta S^\circ = S_f^\circ(d) - 2 S_f^\circ(m) = -154.3 \text{ J/mol/K}$$

$$\Delta G^\circ = \Delta H^\circ - 298 \Delta S^\circ = -60.08 \frac{\text{kJ}}{\text{mol}} - 298 (-154 \frac{\text{J}}{\text{mol/K}}) = -14.1 \frac{\text{kJ}}{\text{mol}}$$

$\Delta G$  negative so spontaneous.

c) Calculate the enthalpy change per hydrogen bond formed in the gas phase. Why isn't a similar calculation useful to estimate the entropy or free energy of hydrogen bond formation?

enthalpy per H-bond  $\sim -30 \text{ kJ/mol}$

for entropy the 1<sup>st</sup> H-bond dimerizes molecules, a big entropy change, the second restricts relative rotation, a smaller effect. Since the two are different processes, shouldn't average them.

Name \_\_\_\_\_

d) We know that for a process to occur spontaneously the entropy of the universe must increase. Dimerization in the gas is spontaneous, yet we are decreasing the disorder (entropy) of the HCOOH molecules. What must be occurring if this process is to occur spontaneously under standard conditions?

The heat given off disorders other things in the surroundings.

e) Calculate the equilibrium constant for the dimerization reaction at a temperature of 50°C (state any assumptions made).

Assume  $\Delta H$ ,  $\Delta S$  temp independent

$$50^\circ\text{C} = 323\text{K}$$

$$\begin{aligned}\Delta G(323) &= -60.08 \frac{\text{kJ}}{\text{mol}} - 323\text{K}(-0.154 \frac{\text{kJ}}{\text{mol}\cdot\text{K}}) \\ &= -10.34 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

$$K = e^{-\Delta G/RT} = e^{+3.85} = 47$$

f) From your knowledge of interactions present in water solutions, do you expect the dimerization of formic acid to be more favorable or less favorable in water solution than in the gas phase? (explain)

less favorable because H-bonds to water will compete with H-bonds between the formic acid molecules.

g) Based on your knowledge of thermodynamics, can you predict whether the gas phase dimerization will be a rapid process? (explain)

thermodynamics does not tell about rates of processes.

Name \_\_\_\_\_

2. A van der Waals gas obeys the equation of state:

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

The thermodynamic behavior of such a gas can be summarized by:

$$dE = C_v dT + \frac{n^2 a}{V^2} dV \quad \text{and} \quad dS = \frac{C_v}{T} dT + \frac{nR}{(V-nb)} dV$$

For the isothermal, reversible compression of a van der Waals gas from initial volume  $V_1$  to final volume  $V_2$ , evaluate  $\Delta E$ ,  $\Delta S$ ,  $\Delta A$ ,  $q$  and  $w$ .

(Leave answers in terms of  $C_v$ ,  $T$ , volumes and any other constants).

$$\Delta E = \int dE \quad \text{since isothermal } dT = 0 \quad \Delta E = \int_{V_1}^{V_2} \frac{n^2 a}{V^2} dV$$

$$= -n^2 a \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$

$$\Delta S = \int dS \quad \text{as above } dT = 0 \quad \Delta S = \int_{V_1}^{V_2} \frac{nR}{(V-nb)} dV = nR \ln \left( \frac{V_2 + nb}{V_1 + nb} \right)$$

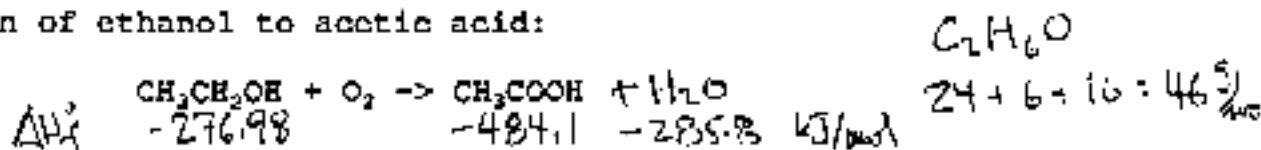
$$\Delta A = \Delta E - T \Delta S \quad \text{use values above}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad \text{so } q_{\text{rev}} = T \cdot \Delta S \quad \text{use } \Delta S \text{ above}$$

$$w = - \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \left[ \left( \frac{nRT}{V-nb} \right) - \frac{n^2 a}{V^2} \right] dV \quad \text{see } \Delta E \text{ \& } \Delta S \text{ above}$$

Name \_\_\_\_\_

3. Some bacteria carry out an aerobic (using  $O_2$  from the air) fermentation of ethanol to acetic acid:



a) If 1 liter of a 1% by weight solution of ethanol was fermented by a growing culture in a perfectly insulated container (e.g. a thermos flask) what would be the final temperature when all of the ethanol is gone if all of the heat from the reaction were liberated into the solution? (assume that the mass of bugs is small compared to the water, get any thermodynamic data you need from tables in the text e.g. p.33 and p.686; state any assumptions that you must make)

751

assume  $T = 298$ 

$$\Delta H_{\text{react}} = \Delta H_f^\circ(\text{acetic acid}) - \Delta H_f^\circ(\text{ethanol}) \quad \text{heat up } H_2O$$

$$= -492.9 \text{ kJ/mol} \quad + \Delta H_f^\circ(H_2O) \quad \Delta H \text{ indep of } T$$

$$1\% \rightarrow 10 \text{ g} / 1000 \text{ g}$$

$$\frac{10 \text{ g}}{46 \frac{g}{mol}} = 0.217 \text{ mol} \rightarrow 107 \text{ kJ liberated into } H_2O$$

$$H_2O \quad C_p = 4.18 \text{ J/K/g} \times 1000 \text{ g} = 4.18 \text{ kJ/K} \quad \text{final } T.$$

$$\Delta H = C_p \Delta T \quad \Delta T = \frac{\Delta H}{C_p} = \frac{107 \text{ kJ}}{4.18 \text{ kJ/K}} = 25^\circ \quad \begin{matrix} 298 \text{ K} \\ \downarrow \\ 323 \text{ K} \end{matrix}$$

b) Typically one would not see all of the heat from such a reaction liberated into the solution - what must have happened to it?

the "bugs" grow, synthesizing new compounds, endothermic reactions absorb some of this heat.

Name \_\_\_\_\_

4. Consider a system which goes from one phase  $\alpha$  to a second phase  $\beta$  at a transition temperature  $T_m$  at constant pressure. For the equilibrium transition one mole of this material absorbs a heat of  $q_m$ . The molar heat capacities for the  $\alpha$  and  $\beta$  phases are  $C_{p,\alpha}$  and  $C_{p,\beta}$  and there is a molar volume change of  $\Delta V$  (all independent of temperature).

a) Evaluate  $w$ ,  $\Delta E$ ,  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  for the process of converting one mole of the system from  $\alpha$  to  $\beta$  at  $T_m$ . (leave answer in terms of the observables and constants given above).

$$w = -\int P dV = -P \Delta V \quad \Delta E = q + w = q_m - P \Delta V$$

$$\Delta H = q_p = q_m \quad \Delta S = \frac{q_m}{T_m} \quad \Delta G = \Delta H - T \Delta S$$

$$\Delta G = 0$$

b) Evaluate  $\Delta S$  and  $\Delta H$  for the process of converting one mole of the system from  $\alpha$  to  $\beta$  at  $T^* < T_m$ .

$$\begin{array}{ccc}
 \alpha & \xrightarrow{T_m} & \beta \\
 C_{p,\alpha} \downarrow & & \uparrow C_{p,\beta} \\
 \alpha & \xrightarrow[T^*]{\Delta H, \Delta S} & \beta
 \end{array}$$

$$\begin{aligned}
 \Delta H(T_m) &= \Delta H(T^*) + C_{p,\alpha}(T^* - T_m) + C_{p,\beta}(T_m - T^*) \\
 &= \Delta H(T^*) + (C_{p,\beta} - C_{p,\alpha})(T_m - T^*) \\
 \Delta H(T^*) &= \Delta H(T_m) + \Delta C_p(T^* - T_m) \\
 \Delta S(T_m) &= \Delta S(T^*) + C_{p,\alpha} \ln\left(\frac{T^*}{T_m}\right) + C_{p,\beta} \ln\left(\frac{T_m}{T^*}\right) \\
 &= \Delta S(T^*) + (C_{p,\beta} - C_{p,\alpha}) \ln\left(\frac{T_m}{T^*}\right) \\
 \Delta S(T^*) &= \Delta S(T_m) + \Delta C_p \ln\left(\frac{T^*}{T_m}\right)
 \end{aligned}$$



Name \_\_\_\_\_

c) The denaturation transition of a globular protein may be modeled as such a phase change. If  $q_m = 638 \text{ kJ/mol}$  at  $T_m$  of  $70^\circ\text{C}$  and

$C_{p,\alpha} - C_{p,\beta} = 8.37 \text{ kJ/mol K}$  ( $T$  independent), calculate  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  for the process of denaturing one mole of this protein (i) at  $T_m$  and (ii) at  $37^\circ\text{C}$ . How much work is required to denature the protein at  $37^\circ\text{C}$ ?

$$\text{at } T_m \quad \Delta G = 0 \quad \Delta H = 638 \frac{\text{kJ}}{\text{mol}} \quad \Delta S = \frac{638 \frac{\text{kJ}}{\text{mol}}}{343 \text{ K}} = 1.86 \frac{\text{kJ}}{\text{mol K}}$$

$$70 - 37 = 33 \text{ K} = T_m - T^*$$

$$\Delta H(37^\circ) = 638 \frac{\text{kJ}}{\text{mol}} - 8.37 \frac{\text{kJ}}{\text{mol K}} \cdot 33 \text{ K} = 361.8 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S(37^\circ) = 1.86 \frac{\text{kJ}}{\text{mol K}} - 8.37 \frac{\text{kJ}}{\text{mol K}} \cdot \ln\left(\frac{343}{310}\right) = 1.01 \frac{\text{kJ}}{\text{mol K}}$$

$$\Delta G = \Delta H(37^\circ) - 310 \Delta S(37^\circ) = 48.7 \frac{\text{kJ}}{\text{mol}} \quad \text{this is effectively work required.}$$

d) If  $\Delta V = -3 \times 10^{-3} \text{ l/mol}$ , will the transition temperature be increased or decreased at 1000 atm pressure relative to 1 atm? Write a thermodynamic cycle which would allow you to calculate the transition temperature at 1000 atm, indicate on it what information you would need to carry out the calculation.

$$\Delta G(P) = \Delta G(1 \text{ atm}) + \Delta V \cdot (P - 1) \quad \text{if } \Delta V = V_\alpha - V_\beta \text{ using convention above}$$

for conversion  $\alpha \rightarrow \beta$

$$\Delta G(P) = \Delta G(1 \text{ atm}) + 3 \times 10^{-3} \frac{\text{l}}{\text{mol}} (P - 1) \quad P > 1 \text{ will}$$

give  $\Delta G(P) > \Delta G(1 \text{ atm})$  trans temp should decrease. To get  $T_m$  need

$$C_p(T, P)$$